ELECTROLYSIS OF MINE DRAINAGE

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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ABSTRACT

Mine drainage in Ohio and surrounding Appalachian regions has significantly impacted watersheds, their aquatic habitats, and caused public health and safety hazards. This is in large part due to the oxidation of pyrite, $FeS_{(s)}$, which is present in underground deep mines and waste tailings (gob) piles. In addition to the production of ferric iron, large amounts of acidity are produced, thus causing acid mine drainage (AMD). The acidity and ferric hydroxide sludge that is generated is toxic to aquatic organisms and also clogs drains and channels, presenting hazards to the public. Active treatment methods usually consist of aeration or chemical oxidation, alkaline chemical addition, and clarification (settling). Among these, ferrous iron oxidation is the most critical step for treatment of high iron AMD sources. Using electrolysis to drive this chemical change has many advantages over traditional methods. The study is to determine how electrolysis can be used to treat AMD, determine its feasibility as a treatment system, and gage its ability to produce marketable products. This study also includes producing a pilot scale unit that demonstrates the capabilities of using electrolysis technology at AMD sites in Ohio. The pilot project was designed to treat 1 gpm of Truetown Seep AMD, with the goal of proving scalability and providing more in-depth engineering data for the design of a full-scale treatment plant. The electrolysis pilot unit was able to remove 99% of iron with sodium hydroxide dosing, 20 minutes of electrolysis, and 90 minutes of clarification. The electrolysis treatment was able to oxidize ferrous iron in a manner that was rapid and produced useable by-products. In conclusion, this study and pilot test has successfully shown that the electrolysis of mine drainage is a scalable, viable treatment method for AMD.
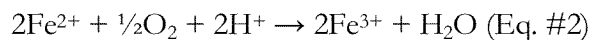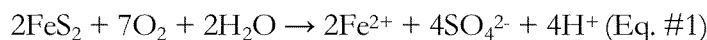
BACKGROUND

Iron in Mine Drainage

Mine drainage in Ohio and surrounding Appalachian regions has significantly impacted watersheds, their aquatic habitats, and caused public health and safety hazards. This is in large part due to the oxidation of pyrite, $FeS_{(s)}$, which is present in underground deep mines and waste tailings (gob) piles, through the following steps:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \text{ (Eq. \#1)}$$

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \text{ (Eq. \#2)}$$

In addition to the production of ferric iron, large amounts of acidity are produced, thus causing acid mine drainage (AMD). The acidity and ferric hydroxide sludge that is generated is toxic to aquatic organisms and clogs drains and channels, presenting hazards to the public.

All treatment alternatives for iron-laden AMD consist of a combination of pH adjustment, oxidation of ferrous iron, and settling. This can be done passively, through wetlands, limestone channels, steel slag leach beds, ponds and other methods, or actively through plant style operations. Passive methods all have a proven history of treating mine drainage but are space intensive and can have unreliable effluent water quality with difficulties in operation and maintenance. The largest flow and highest iron concentration mine drainage sites typically require active treatment methods to increase treatment rates, leading to a decrease in the land area required for treatment, and provide reliable effluent. Active treatment methods usually consist of aeration or chemical oxidation, alkaline chemical addition, and clarification (settling). Among these, ferrous iron oxidation is the rate-limiting step (*Jensen, 2003*). Oxidation is necessary for the treatment of AMD because of the significantly lower solubility of ferric iron at a pH below 11, as compared to its reduced ferrous state as shown in the following Figure:
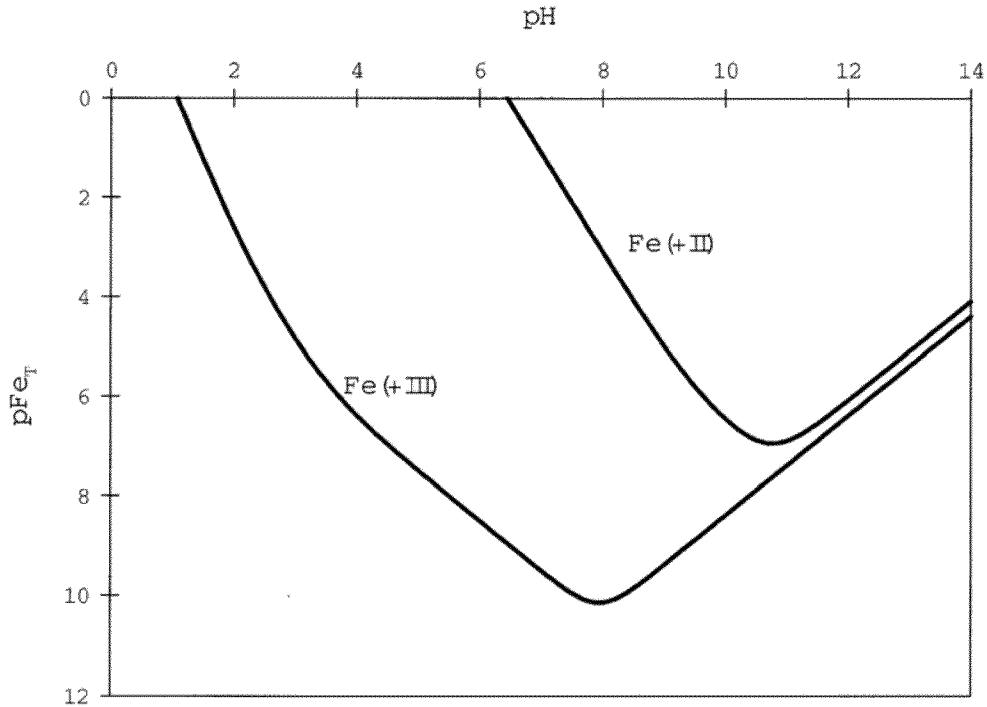
Figure 1: Comparison of the Solubility of Fe^{2+} and Fe^{3+}, (In equilibrium with $Fe(OH)_2(s)$, FeOOH, no dissolved carbonate species) (*Jensen, 2003*).

In active treatment using atmospheric oxygen, iron oxidation is first order between a pH of 5 and 8 and the rate is slow (*Jensen, 2003*). These systems require either a large surface area pond for passive aeration, blowers, or large pumps to spray or use a Venturi. When chemicals are used for iron oxidation, costs are typically high, and depending on the agent used, can leave residuals such as chloride or manganese. These materials are hazardous to handle and present liability and logistical issues while transporting them to a treatment site.

Electrochemistry and Mine Drainage
Electrochemistry is a branch of chemistry that studies chemical reactions that take place in a solution at the interface of an electron conductor and an electrolyte (*Ebbing, 2007*). Causing these chemical reactions by forcing an electric potential difference across the electrolyte is known as *electrolysis*. The electrolysis of mine drainage has many advantages over other oxidation methods. First, the main reagent used is the electron, considered "clean" since it leaves no residuals. Electrochemical processes are versatile; they can be altered dramatically with electrode materials, electrode configurations, and cell potentials. Scalability is straightforward as the electrochemical cell configuration can often be maintained for flows ranging from microliters to thousands of gallons per minute. Electrochemical processes are

2

safe due to the mild conditions typically employed, and the minor addition of chemicals that may be needed. Lastly, the materials needed to build electrochemical treatment cells are readily available and very little, if any, specialized equipment is needed (*Rajeshwar, 1997*).

The change from Fe^{2+} to Fe^{3+} is a reduction-oxidation (redox) reaction, which is simply a transfer of electrons. The reduced ion gains electrons, while the oxidized ion loses electrons. This transfer of electrons lends itself well to being controlled via an electrochemical cell. The redox pair ($Fe^{2+} \square Fe^{3+}$) has a standard electrode potential of +0.77 Volts (V) and has a positive Gibbs free energy, meaning it is thermodynamically favorable under standard conditions (*Jensen, 2003*). This value is obtained by the method shown in the following diagram:
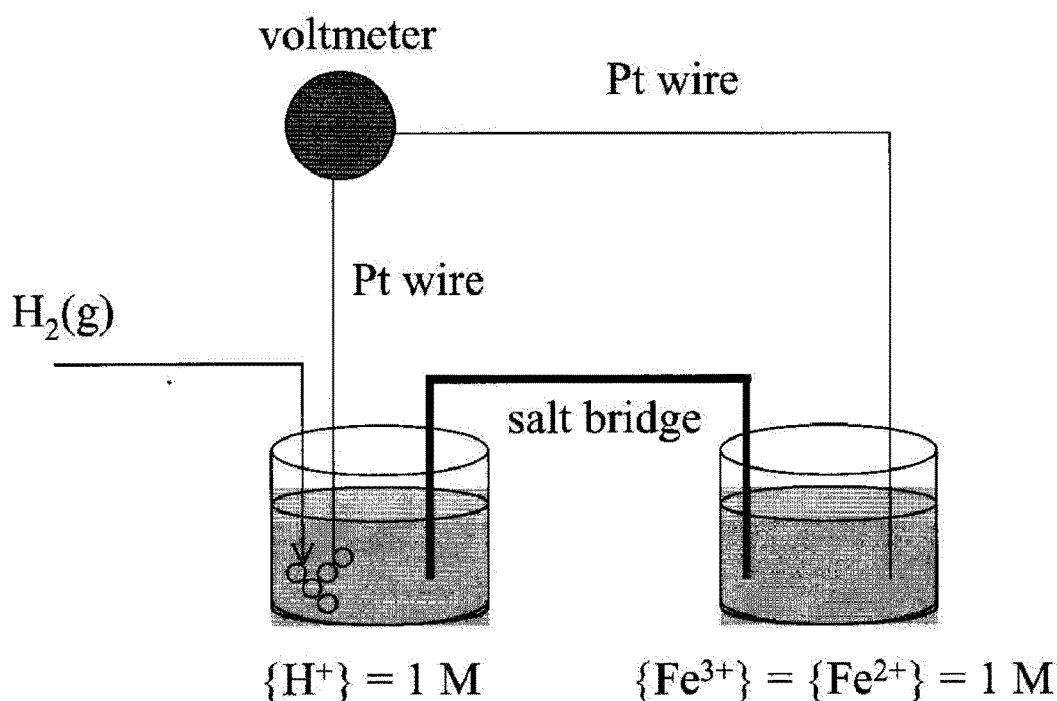
Figure 2: Electrochemical Cell Showing the Standard Hydrogen
Electrode for Fe^{2+} to Fe^{3+} (*Jensen, 2003*).

The voltage required to drive the oxidation of ferrous iron in practice is higher than the standard value due to effects known as overpotential. Overpotential is a combination of ohmic, activation, and concentration effects. In the application of the electrical potential to the solution, there are two points of electrical connections to the electrolyte, known as electrodes, the *anode* and the *cathode*. In electrolysis, the anode is the positive terminal in which the current flows into the electrode from the potential source and oxidation of the ions in solution takes place. In contrast, the cathode is the negative terminal in which the current

3

flows away from the electrode towards the potential source and reduction of the ions in solution takes place.

The application of electrolysis to mine drainage has been studied several times over the last 30 years with the majority of these focusing on the reduction of H^+ ions in solution to H_2 gas at the cathode (see Eq. #7). This produces a rapid rise in pH and can be used to treat the acidity of mine drainage directly with no chemical addition. All experimental work, Treharne and Wright, Friedrich and Knappnik, and Chartrand and Bunce, have used divided cells in their work, with the exception of the first AMD electrolysis experiments by Tyco Laboratories, which used an open cell design. Tyco Labs considered the Fe^{2+} to Fe^{3+} oxidation as the anode reaction, but with an undivided cell at low pH values, there is a back reduction of Fe^{3+} to Fe^{2+} and the pH gain at the cathode is lost due to the pH drop at the anode. Since these first experiments by Tyco Labs in 1972, the focus of research has been on divided cells to prevent this loss of pH increase and cathodic reduction of ferric iron.

The first divided cell work, by Treharne and Wright, used a sand barrier to divide the anode and cathode cells. These experiments used synthetic AMD that flowed into the cathode cell, which raised pH, and $Fe(OH)_3$ then precipitated outside the electrolysis cell. Dilute sulfuric acid was used as the electrolyte in the anode cell, and it was found to "produce higher strength sulfuric acid for use elsewhere" (*Chartrand, 2003*). Chartrand postulated that this was unlikely due to the ability of H^+ and OH^- ions to migrate through the barrier. This is because the sand barrier in this setup acts only as a barrier to convective flow, not conductive or diffusive flow of ions. Friedrich and Knappnik divided their electrolysis cell using ceramic or ion exchange membranes and used the cathode cell to raise the pH. The ion exchange membranes prevented the flow of fluid and the flow of ions between the two cells, with the exception of the exchange ions (i.e. cations or anions). Synthetic AMD with dissolved Fe^{3+} was added to the cathode cell. $Fe(OH)_3$ precipitated in the cell due to the increase in pH, which was then separated from the electrolyte outside the cell (*Chartrand, 2003*). Chartrand and Bunce then followed with their own work using a similar experimental setup as Friedrich and Knappnik and were able to remove iron, nickel, and copper from synthetic and authentic AMD streams via a pH rise in the cathode. The anode and cathode cells in these experiments were 3 mL each and were separated using ion exchange membranes (*Chartrand, 2003*). After the synthetic AMD left the cathode cell, the flow was then heavily aerated (sparged) to oxidize Fe^{2+} to Fe^{3+}, causing the precipitation of $Fe(OH)_3$ and the removal of the iron from the flow.

Electrolysis Reactor Design
All of the previous work using electrolysis to treat mine drainage used the cathode to treat the *acidity* of the mine drainage. The metals removal resulted directly due to the pH rise. This was the sole removal technique with the exception of Chartrand, which followed the electrolysis with oxidation via atmospheric oxygen from air sparging. This study of the electrolysis of mine drainage focuses on the *anode* reaction and its ability to oxidize ferrous iron.

In designing an electrochemical cell for the oxidation of ferrous iron at the anode, the ideal cell passes maximum current per unit volume directly through the Fe^{2+} ions with minimum ohmic (voltage) drop and side reactions.

4

Ohmic losses occur due to the electrolysis system's resistance to the flow of electrons between the power supply and the ions of interest. These occur within the electrolyte, electrode, and in the wiring to the power supply. Ohmic losses are a drop in voltage due to Ohm's law:

$$V=IR \quad \text{(Eq. \#3)}$$

where V = voltage measured in volts (V), I = current measured in amps (A), and R = resistance measured in ohms ($\square$). The power consumed by the electrolysis is the following:
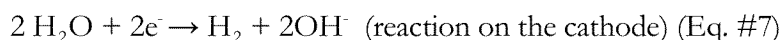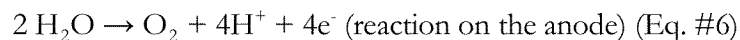
$$P=VI+\square \quad \text{(Eq. \#4)}$$

where P = power measured in watts (W), and $\square$ = power loss due to electrochemical reactions. The V*I term is the power consumed by the Ohmic loss of the system. $\square$ is a function of amperage, with a threshold voltage (similar electrical behavior to a transistor). This threshold voltage is discussed previously, referred to as the standard electrode potential. The resistance of the electrolyte (or AMD) is measured either directly as electrical conductance in units of ohms per unit length of electrolyte, or more commonly in the aquatic chemistry field as specific conductance, the inverse of the electrical conductance, measured in micro-siemens ($\square$S) per unit length. The electrode resistance is a function of electrode material, the cross sectional area of the electrode, and the travel length between the wiring connection and the point of transfer of the current to the electrolyte. Lastly, resistance of the wiring and connections of the system are simply a sum of the components and should be designed to be minor in comparison to the resistances of the electrode and electrolyte.

In designing an electrolysis reactor, ohmic losses (IR) in the system can be significant because the magnitude of the current indicates the reaction rate; i.e. the higher the current, the faster the reaction rate. This is according to Faraday's 1st Law of Electrolysis, which states, "The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode." Faraday's 2nd Law of Electrolysis states, "For a given quantity of electricity, the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight." Combined into their mathematical forms, and simplified for a constant current, the laws take the following mathematical form:

$$n \, \square \, \frac{Q}{Fz} \quad \text{(Eq. \#5)}$$

Where n = number of moles altered by electrolysis, Q = total charge passed through the substance, F = Faraday's constant = 96,485 C/mol (coulombs per mole), z = valence number or number of ions transferred per ion. The conclusions of these laws for the engineering of an electrolysis cell is that since the engineered reactor will convert the ion of interest as rapidly as possible, it is necessary to drive as much electricity (i.e. amperage) through the electrolyte as possible.

5

The other losses in the electrolysis cell are side reactions that take place in the electrolyte which are not intended. The most significant side reaction in the electrolysis of an aqueous solution is the breakdown of the solvent (water):

$$2\,H_2O \rightarrow O_2 + 4H^+ + 4e^- \text{ (reaction on the anode) (Eq. \#6)}$$

$$2\,H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (reaction on the cathode) (Eq. \#7)}$$

As previously discussed, Equation #7 is what was used in prior electrolysis treatments of mine drainage. In a reactor where the anodic oxidation of ferrous iron is the reaction of interest, these side reactions affect the efficiency due to the amount of current used in the side reaction. In the electrolysis of mine drainage, these side reactions consume a significant portion of the current, but produce hydrogen and oxygen gas. These reactions can be useful in other electrochemical cell setups, as discussed previously.

There are several additional factors to consider in designing an electrolysis reactor for acid mine drainage. These include mode of operation, electrode geometry, electrode motion, electrode connections, electrode gap, cell division, applied voltage, and current distribution. These factors play an important role in the design decisions for an electrolysis reactor. Ultimately, the engineering and design of any system will be a balance of economics, maintenance, simplicity, reliability, and a host of many other non-engineering related project decisions.

Engineering a Reactor for AMD
Part of the goal of this study is to produce a pilot scale unit that will demonstrate the capabilities of using electrolysis technology at AMD sites in Ohio. The treatment unit is optimized for iron removal, to minimize maintenance and operations complexities, and to increase the potential for marketable by-products.

To meet these needs, an undivided, baffled CSTR, with stainless steel plate electrodes was chosen for the electrolysis reactor. Stirring or mixing is primarily achieved through gas production and electrolyte turbulence (Reynolds Number). The undivided cell, where the anode and cathode electrolyte solutions are able to mix freely, has in the past been considered to be a poor choice, because Fe^{2+} to Fe^{3+} oxidation rates would be hampered by the back reaction at the cathode of Fe^{3+} to Fe^{2+} reduction. In the electrochemical industry this reduction is utilized to continually regenerate ferrous iron, known as Fenton's reagent, for the treatment of environmental contaminants such as chromium and organic waste streams. While this back reaction is well known, the cathodic reduction is strongly pH dependant and can be avoided with adequate pH control as shown in the following diagram:

6
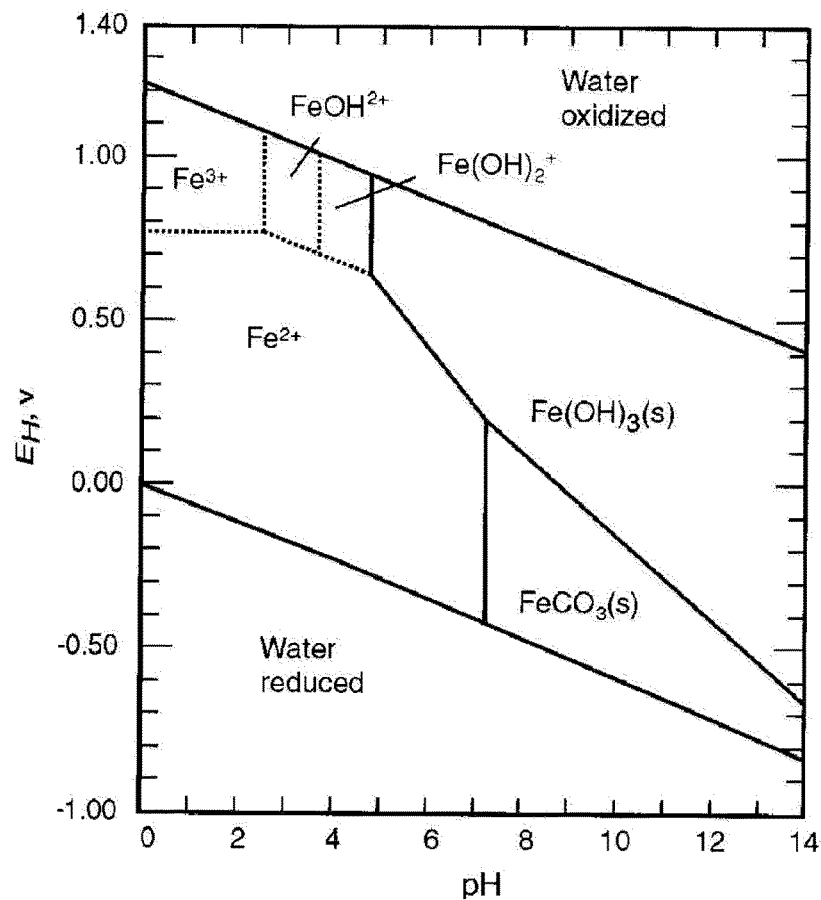
Figure 3: Forms of Iron in Water as a Function of Redox Potential Vs. pH, Total Iron Activity 10^{-7}, 96 mg/L SO_4^{-2}, CO_2 species at 1000 mg/L H CO_3^-, Std. Conditions (*Crittenden, 2005*)

It is evident that the electrolytic reduction of ferric iron does not become a factor at a pH above 7. The formation of $FeCO_3$ generally does not occur because of its solubility constant relationship with $Fe(OH)_3$. Since Fe^{2+} is unlikely to cathodically reform at a pH above 7, an undivided setup was chosen with pH control via chemical addition. This simplifies the setup and decreases capital and maintenance costs of the system. For these reasons, the pH of the reactor in operation should be above 7 at all times. Additionally, the stability of the iron hydroxide floc is pH dependent as shown in the following diagrams:

7

Figure 4: Solubility Diagram for Fe^{3+} and the Relationship to the Operating Range for Use as a Coagulant in Water Treatment. (*Crittenden, 2005*)

Equations used for constructing plot:

$$\log [Fe^{+3}] = 3.2 - 3pH$$

$$\log [FeOH^{+2}] = 1.0 - 2pH$$

$$\log [Fe(OH)_2{}^+] = -2.5 - pH$$

$$\log [Fe(OH)_4{}^-] = -18.4 + pH$$

Figure 5: Operating Range for Fe^{3+} Coagulant in Water Treatment. (*Crittenden, 2005*)

8

As shown in Figures 4 and 5, there are optimum pH ranges in the use of $Fe(OH)_3$ as a coagulant, which mirrors the process of removal from AMD by f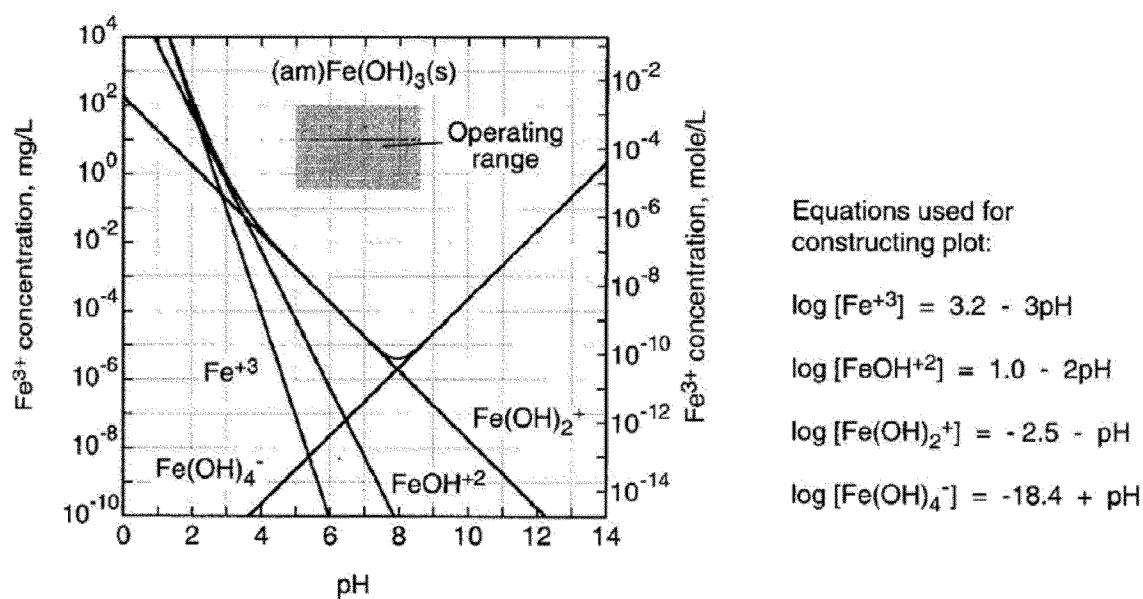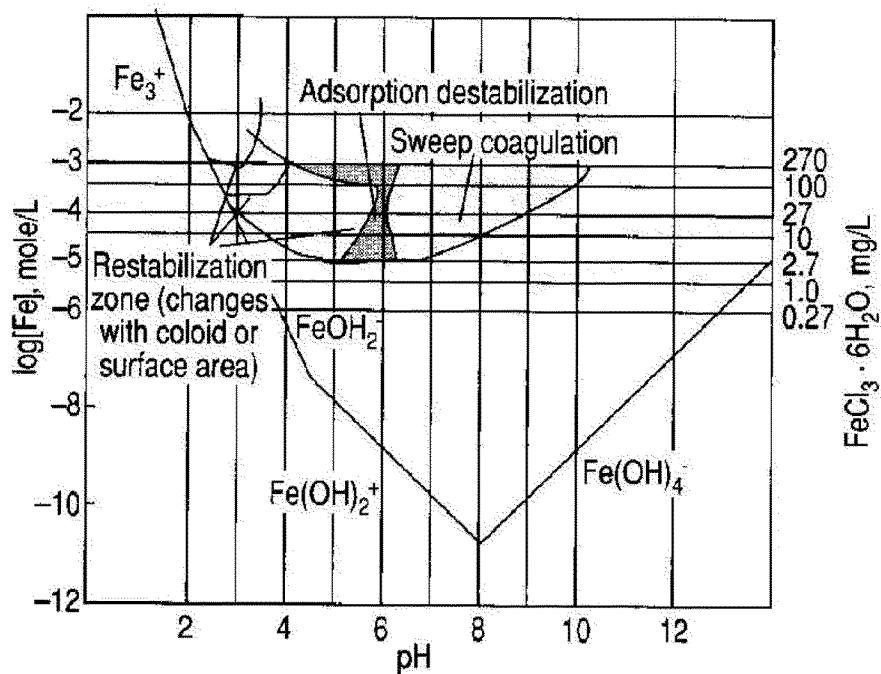locculation and precipitation. This optimum pH, 7.5 to 8, corresponds to the minimum pH needed to prevent the reduction of ferrous iron and the minimum solubility of $Fe(OH)_3$. One will also notice in Figures 4 and 5 that there are minimum iron concentrations for an adequate floc, so the pilot project will also include a sludge recirculation to increase iron concentrations, thus improve settling characteristics of the floc in the clarifier.

The electrode connections for the pilot project will be mono-polar, in order to keep the applied voltages low for safer operations. In designing a full-scale treatment plant, it may become ideal to switch to a bi-polar wiring configuration to decrease induced magnetic fields and physical connections to electrodes. There is also evidence that the bi-polar wiring configuration offers a power savings (*Rajeshwar, 1997*), although the reasons for these savings are not immediately clear. Because of the mono-polar configuration in the pilot-project, an applied voltage of ~13-15 volts was used. This was high enough overvoltage to drive iron oxidation reactions, low enough for a safe working voltage, and was convenient because of the ability to obtain manufactured power supplies.

The electrode gap for the pilot project will be held to 2 inches. This is due to the success with prior batch tests (the details and results of these preliminary batch tests will be discussed later), which indicated 2 inches is sufficiently close to drive the reaction rapidly. Additionally, the gap was large enough to allow the ability to maintain the reactor and observe the electrolyte during treatment, as well as provide a safe buffer between plates to prevent short-circuiting or arcs. Stainless steel plate electrodes (Type 304) were used because of their corrosion resistance and their widespread availability. The stainless steel plates, although thin, have enough rigidity to maintain an even electrode gap. This results in well-distributed current, however, the disadvantage to using stainless steel is that it is a relatively poor conductor compared to either copper or aluminum and less corrosion resistant than gold or platinum. Thus copper distribution busbars were used to decrease resistance from the wiring connection to the point of current transfer to the electrolyte.

The goals of the pilot project, combined with the previously discussed design decisions, resulted in the pilot project setup that will be presented in the next chapter. The bulk of the research available on the electrolysis of mine drainage has been presented here in these previous sections as well as referenced in the Bibliography. Because of the limited literature and design resources for these systems, a large portion of this process has been experimental in nature. The pilot project takes a look at what may be possible with the use of such techniques in the future.

PILOT PROJECT

Experimental Background
The pilot project design was prefaced by a series of controlled bench-scale experiments, which produced practical and analytical insight into the anodic oxidation of ferrous iron in AMD. As previously indicated, the experimental work also showed that the iron oxidation reaction rates are improved with increasing current densities, pH, electrode area, and electrolyte Reynolds number (turbulence). The preliminary experiments led to the development of a small 2.5-gallon SBR. The batch unit used four stainless steel plates in a parallel configuration. With the addition of crystallized NaOH addition to increase the pH to 8, the batch unit was able to treat high iron AMD effectively.

The results from an example SBR setup are listed below. The test was on AMD from Rehoboth Gob (Site #3004). The results are as follows:

Table 1: Rehoboth Gob AMD Batch Test Results			
Parameter	**Units**	**Pre-Treatment**	**Post-Treatment**
Aluminum, Total	mg/L	111	0.289
Calcium, Total	mg/L	355	309
Iron, Total	mg/L	978	0.568
Potassium, Total	mg/L	32.3	33.3
Magnesium, Total	mg/L	138	120
Manganese, Total	mg/L	20.5	5.1
Sodium, Total	mg/L	22.8	1210
Hardness, Total	mg/L	1455	1266

All Results Non filtered

The Rehoboth batch test received 90 minutes of electrolysis. The pH was initially adjusted from 3.5 to 7.5 using crystallized NaOH. The power supply delivered 6 amps at 9 volts. The pH was adjusted a second time to 7.5 in the middle of treatment. Clarification time was 20 minutes after electrolysis ended. Good settling characteristics were observed with the Rehoboth Gob batch test, presumably due to increased iron hydroxide levels, as shown previously in Fig 5.

Based on the literature and experimental background, the design parameters had been adequately refined to proceed to building a pilot scale treatment unit.

10

Site Selection

The use of electrolysis to treat AMD is most suited for high iron flows due to improved mass transport and settling characteristics, as well as conventional methods becoming less viable options. For these sites, passive methods are land intensive, aeration rates slow, and chemical oxidants expensive. An example of this type of site is the Truetown Seep located in Athens County, Ohio. The mine flow is located behind a group of homes, so space is limited, and the average flow rate is 830 gpm, which causes and iron loading in Sunday Creek of 2 tons per day. The mine flows out of a sealed pump station that ruptured in 1984. The area required for passive treatment is too large, and a doser would fill Sunday Creek with sludge. The flow impacts the last seven miles of Sunday Creek, a 139 square mile watershed, until its confluence with the Hocking River (*Riefler, 2007*). The Truetown Seep is an ideal application for electrolysis, because the high iron levels (~380 mg/L) can be rapidly oxidized and settled, and thus the metals loadings removed from the flow.

Materials and Methods

The pilot project was designed to treat 1 gpm of Truetown Seep AMD, with the goal of proving scalability and providing more in-depth engineering data for the design of a full-scale treatment plant. The materials required for the tests are as follows; this does not include typical construction supplies such as lumber, nails, plumbing and wiring supplies, as well as any equipment required for sample analysis and electrical data acquisition.

Table 2: Pilot Project Materials			
Item	**#**	**Manufacturer/Supplier**	**Purpose**
45 Gallon Molded Polyethylene Tank, 36"X24"X12"	1	Tamco	Electrolysis Reactor Tank
90 Gallon Molded Polyethylene Tank, 36"X24"X24"	1	Tamco	Clarification Tank
Polyethylene Cover for Tanks	2	Tamco	Safety and Gas Collection
Variable-Speed Peristaltic Pump, Med. Flow - 0.4 to 85 mL/min.	1	United States Plastic Corp.	NaOH Chemical Feed
High Density Polyethylene Sheet, 1/8"X24"X36"	1	United States Plastic Corp.	Spacer for Electrodes
High Density Polyethylene Sheet, 1/4"X24"X36"	1	United States Plastic Corp.	Baffle and Spacers for Electrodes
Grounding Rod 1/2" Diameter X 8' Long	1	McMaster-Carr	Grounding

11

Harsh Environment, High-Amp Distribution Bar, 130 Amps	2 McMaster-Carr	Electrical Distribution
2.1 gpm Diaphragm Pump, 12V	1 High Flo	Sludge Pump
1 gpm Diaphragm Pump, 12V	1 High Flo	Inflow Feed Pump
304 Stainless Steel Plates, 12-5/8"X33"X22 Gauge	12 Knowlton Industrial Steel	Electrodes
70 Amp, 13.8 Volt DC Linear Power Supply w/ Amp &Volt Meters	2 Astron	Power Supply for Electrolysis and Pumps
Copper (Alloy 110), 1/16" X 5/8" X 33"	12 McMaster-Carr	Current Distribution Across Steel Plates
32 Gallon Black Trash Can	1 Rubbermaid	Sludge Collection and Dewatering
50% NaOH (20 Liter hardpack)	1 ODNR Cambridge Environmental Lab	pH adjustment

The electrolysis unit was sized to provide 45 minutes hydraulic residence time (HRT) at 1 gpm. This minimum residence time was obtained from the prior batch tests. NaOH feed rate was calculated to be ~2.5 gal per day, based on batch run chemical additions and acidity calculations. The clarifier was sized for a HRT of 90 minutes. Experimentally, a HRT of 20 minutes is required for settling, but water treatment parameters recommend as long as 4 hours HRT. The clarifier overflow rate was 288 gpd/ft^2 for the single pass setup, and 864 gpd/ft^2 with sludge recirculation at 2 gpm. Weir overflow rate was 23,000 gpd/ft.

AMD from Truetown was collected and trucked back to the Cambridge DMRM AML office in a 500-gallon water tank with a sealed lid (to minimize aeration of the water during transport), then pumped through the electrolysis pilot unit at 1 gpm. During the testing, sludge was recirculated from the clarifier back to the electrolysis unit at 2 gpm.

Sampling Plan (Co-Authored by Jeff Calhoun, DMRM)
The pilot project sampling follows OEPA sampling protocol (Manual of Ohio EPA Surveillance Methods and Quality Assurance Practices, 2009) for chemical water quality (WQ) monitoring. This includes collecting water quality (grab) samples, which are preserved and delivered (within 36 hours) to the ODNR-DMRM Cambridge Lab for analysis of Group 1, Group 2, and Additional Metals parameters. Constituents are measured onsite with a YSI Multimeter as listed below:

Table 3: Water Quality Testing Parameters			
Group 1	*Group 2*	*YSI Parameters*	*Additional Metals*
Acidity (total)	Phenolphthalein Alk. as CaCO3	PH	Nickel
Alkalinity (total)	Carbonate Alk. (CO3) as CaCO3	DO	Chromium
Aluminum (total)	BiCarbonate Alkalinity as CaCO3	ORP	
Calcium (total)	Hydroxide Alkalinity as CaCO3	TDS	
Hardness (total)	Total Solids	Conductivity	
Iron (total)	Chloride (total)	Temperature	
Magnesium (total)	Sodium (total)		
Manganese (total)	Potassium (total)		
PH	Total Cations (EPM)		
Specific Conductivity	Total Anions (EPM)		
Sulfate (total)	Measured TDS		
Dissolved Solids (total)	Calculated TDS		
Suspended Solids (total)	Carbonate Hardness		
	Non-carbonate Hardness		

Test Pilot Water Quality Data Collection - Grab samples will be collected during the pilot tests at 6 locations (see Figure 6) to provide data on the effectiveness of the electrolysis treatment method. Along with onsite sampling of the source water, grab samples will be collected 45 minutes after system startup and every 45 minutes thereafter for a total of 6 hours. A grab sample will also be collected to measure ferrous iron concentrations. All grab samples will be preserved and delivered the DMRM lab to be analyzed for the parameters in Table 4. Throughout the experiment, continuous monitoring of pH, specific conductivity, temperature, dissolved oxygen, and oxidation reduction potential will take place using a YSI multimeter at the YSI sample location (see Figure 6).
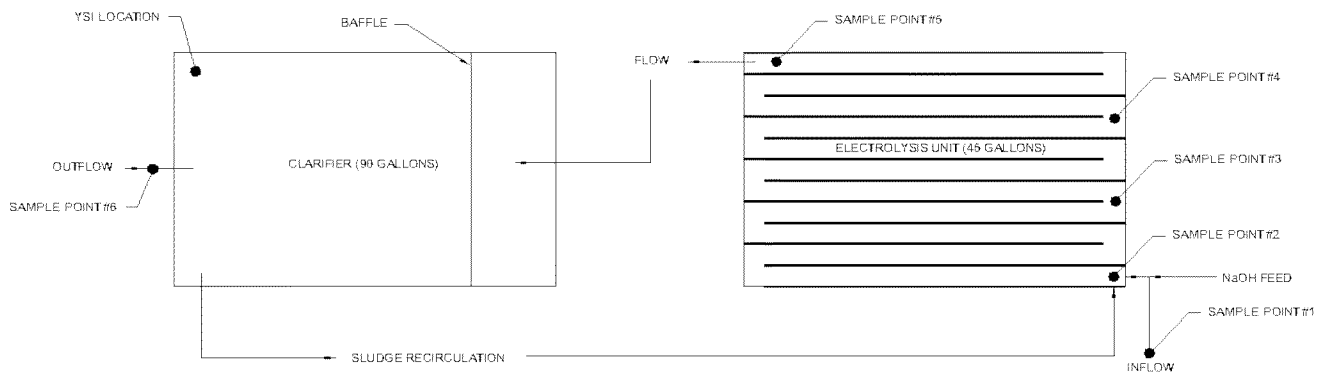
13

Figure 6: Water Sampling Locations for Pilot Unit Test

Control - Adjusting the pH of the mine water and pumping the water through the pilot unit without applying an electrical current will establish experimental control. After 1.5 hours of operation, one grab sample will be collected at sample point # 6 (Figure 6) and analyzed.

Quality Control/Quality Assurance - One duplicate grab sample will be collected at each sample location, and one field blank grab sample will be collected during the 6-hour pilot unit operation.

Test Pilot Electrical Data Collection – Voltage and amperage will be measured during the pilot test for the whole system via the electrical meters on the two (2) power supplies, as well as measured for each individual plate using a clamp-on amp meter and a handheld multimeter to measure voltage.

Electrode Corrosion Test
The electrolysis pilot unit utilizes stainless steel plates as the anode and cathode. In order to avoid elevated metal readings in the mine water after electrolysis has been applied, it is necessary to detect any metals that are derived from the stainless steel plates during the electrolysis application. For this analysis, tap water (Source: Guernsey County Municipal Water) was used as the electrolyte as it has some conductivity with little to no dissolved metals. No pumps ran during the test, and the clarifier was not connected. Samples were sent to the DMRM lab in Cambridge for metals analysis. Metal parameters measured will include metals that are associated with mine water, such as iron (Fe) and manganese (Mn), as well as metals that are associated with stainless steel, which include chromium and nickel. These metals levels are important because they indicate plate corrosion, in particular, the anode. The test used tap water as the electrolyte. Samples were taken at the start, 15 minutes, and 30 minutes subsequent to startup. Additionally, pH, dissolved oxygen (DO), and temperature were measured using a YSI multimeter.

Yellow precipitate (ferric iron) was observed forming at higher concentrations as the test proceeded. In addition, a white deposit (presumably a calcium product) was found on the

14

cathode. These observations were confirmed by the sampling results. No pitting or corrosion could be observed on the anode, although since the sampling data from the start of the test shows no measurable dissolved iron, all of the iron came from the oxidation of the anode. It is believed that the calcium deposits were from the localized pH increase from the cathodic reduction of H^+ to $H_{2(g)}$. The high dissolved oxygen levels, upwards of 250% normal DO saturation limit, are a result of the pure $O_{2(g)}$ that is generated on the anode. This test also served as an electrical systems test prior to the pilot run. All electrical systems operated satisfactorily and no changes were needed. The results are as follows:

| Table 4: Pilot Project Corrosion Analysis Test Results				
Parameter	**Units**	**t = 0 min**	**t = 15 min**	**t = 30 min**
Temperature	Deg. C	23.25	24.88	24.59
PH	SU	7.51	7.54	7.37
Spec. Conductivity	µS/cm	1180	1170	1140
Dissolved Oxygen	mg/L	4.54	12.94	18.51
Total Acidity as CaCO₃	mg/L	3.58	4.59	5.57
Total Alkalinity as CaCO₃	mg/L	184	173	151
Total Dissolved Solids	mg/L	793	782	764
Total Suspended Solids	mg/L	2	9	16
Sulfate	mg/L	370	364	372
Chloride	mg/L	28.9	29.1	28.9
Calcium	mg/L	78.1	73.6	65.8
Magnesium, Total	mg/L	36.9	37.9	37.5
Sodium	mg/L	118	119	118
Potassium	mg/L	3.87	3.87	3.84
Iron, Total	mg/L	<0.050	2.9	6.96
Manganese, Total	mg/L	<0.030	0.055	0.092
Aluminum, Total	mg/L	0.71	0.72	0.674
Chromium, Total	mg/L	<0.050	0.638	1.67
Nickel, Total	mg/L	<0.050	0.305	0.779
Hardness, Total as CaCO₃	mg/L	347	340	319

All Samples Non Filtered

RESULTS AND DISCUSSION

Pilot Test

The pilot test was conducted at the Ohio Department of Natural Resources Abandoned Mine Land Office in Cambridge, Ohio. AMD from the Truetown site was collected in a 500-gallon tank and transported back to the office on Wednesday October 27, 2010. A sample was obtained from the source at this time. An in-tank sample was taken the morning of the pilot test, Friday October 29th, to determine what impacts occurred to the sample water from transport and storage.
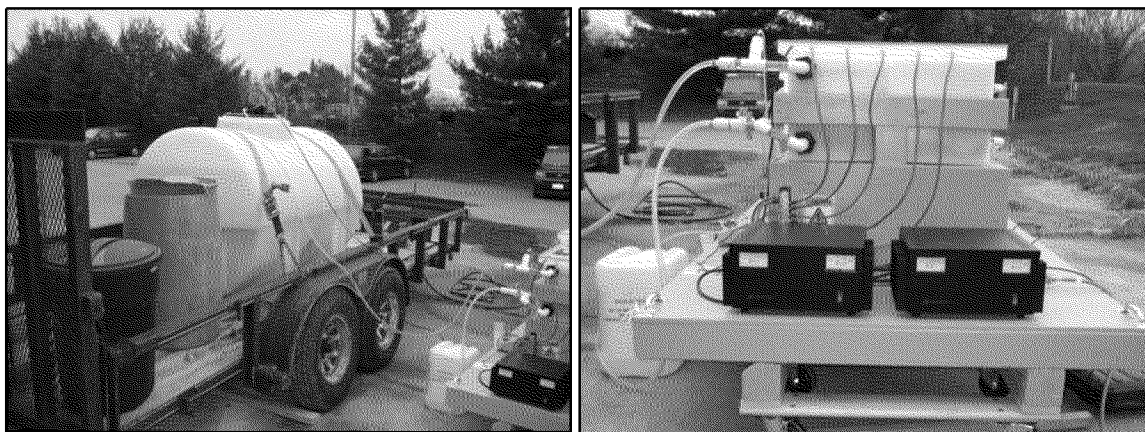
The test began at 7:30 AM with a 1 gpm feed rate from the tank and no sludge recirculation. Sludge recirculation began approximately 3 hours later, at 10:30 AM. Inadequate iron hydroxide precipitate in the system caused poor clarification until approximately 11:30 AM, when iron hydroxide concentrations from the recirculation of the sludge produced proper flocculation and settling in the clarifier. Additionally, the colder temperatures ($\sim40\square$F) initiated gelling of the NaOH solution in the chemical feed lines. Erratic pH control in the pilot unit continued until the problem was resolved by placing the chemical feed tank in a hot-water bath. This took place at approximately 10:30 AM, after which, the electrolysis pilot reached operational equilibrium. At this point proper oxidation of the iron hydroxide took place, as seen in the following picture:

16
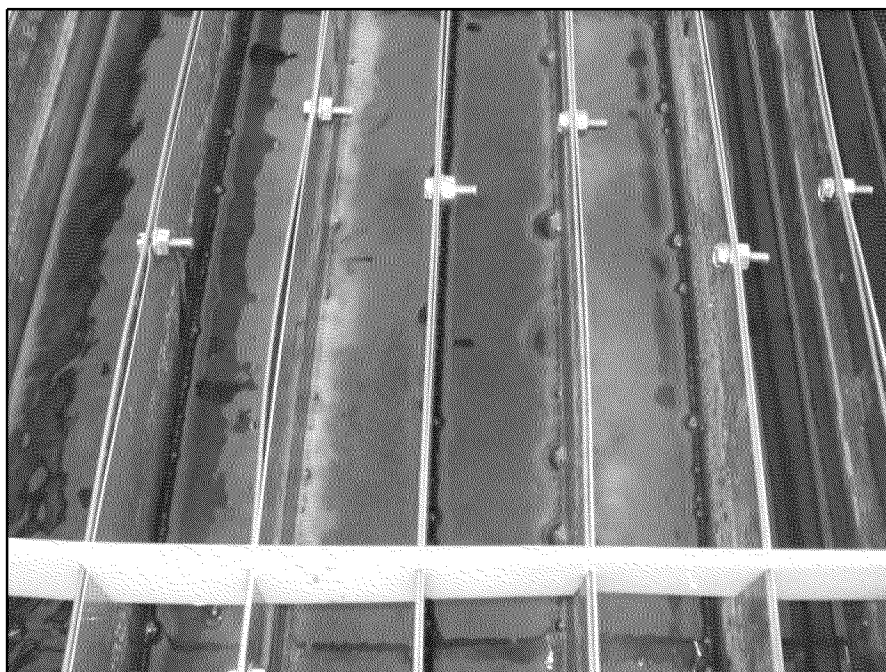
This picture shows the influent, pH adjusted AMD, flowing in from the left, and flowing through the electrolysis cells to exit off of the picture on the right. Full oxidation appeared to have taken place by the 4th cell as indicated visually by the color change from blue to reddish-brown.

The last 6 plates were disconnected to prevent excess power draw from the power supplies. The resulting total amperage draw was 82 amps at 14.5 Volts. The amperage draw from the pumps was 10 amps. The plate amperages, plates 1-6 respectively, were 12.5 A, 28.2 A, 33.4 A, 33.0 A, 33.9 A, and 17.0 A. Plates 2-5 transferred approximately twice the amperage as the end plates because of supplying 2 cells, and plate 1 was less than plate 6 due to an increase electrode gap to accommodate the influent piping. Lastly, the total amperage measured on the plates was approximately twice the supplied, as it measure both the in and out amps (i.e. the anode and cathodes).

The pilot unit operated for approximately 3.5 hours until 2:00 PM when 1 set of samples were taken. The results are as follows:

Table 5: Pilot Project Test Sampling Results

Parameter	Units	1 (Influent NF)	2 (NF)	3 (NF)	4 (NF)	5 (NF)	6 (Effluent NF)	6 (Effluent F)
Temperature	Deg. C	10.4	-	-	-	-	12.98	12.98
pH	SU	5.58	10.2	10.7	10.3	9.92	10.1	10.1
Spec. Conductivity	µS/cm	3027	4140	4130	4130	4130	3959	3959
Dissolved Oxygen	mg/L	2.64	-	-	-	-	2.5	2.5
Total Acidity as $CaCO_3$	mg/L	633	0	0	0	0	0	0
Total Alkalinity as $CaCO_3$	mg/L	12.8	860	1288	573	833	79.2	79.2
Total Dissolved Solids	mg/L	3000	2640	2480	2820	2720	2820	2820
Total Suspended Solids	mg/L	20	2840	3450	2410	2810	51	51
Sulfate	mg/L	1910	1976	2000	1893	1959	1860	1860
Chloride	mg/L	22.3	27.9	28.4	26.8	27.3	22.4	22.4
Calcium	mg/L	212	247	292	230	332	50.2	47.3
Magnesium, Total	mg/L	70	128	155	91.8	118	10.4	9.93
Sodium	mg/L	229	843	841	859	846	851	858
Potassium	mg/L	12.2	12.4	12.4	12.5	12.6	12.8	12.6
Iron, Total	mg/L	330	683	773	451	619	3.1	<0.050
Manganese, Total	mg/L	6.28	13.1	15.2	8.52	11.3	0.073	<0.030
Aluminum, Total	mg/L	2.06	4.55	5.26	2.95	3.98	<0.050	<0.050
Nickel, Total	mg/L	<0.05	0.39	0.496	0.659	1.84	<0.050	<0.050
Chromium, Total	mg/L	<0.05	0.753	0.977	1.44	4.54	<0.050	<0.050
Hardness, Total as $CaCO_3$	mg/L	818	1144	1367	952	1315	168	168

NF = Non Filtered, F = Filtered

Additionally, as seen in the difference between the filtered and non-filtered effluent samples, there were some suspended iron particles that were transported into the effluent. This was due to an inadequate weir length and too deep of stored sludge volumes in the clarifier. YSI measurements were not taken for locations 2-5 to prevent electrical interference with the YSI instrumentation.

Based on the results from the pilot test, it was determined that to increase clarifier performance, an overflow weir should be constructed across the tank, to decrease the WOR as discussed previously.

Applications to Full-Scale Treatment
To scale the pilot unit to a full-scale facility, only a linear scale up is needed to determine the minimum sizing for the treatment and clarifier units. A full-scale electrolysis treatment unit would need to match the same residence time; more specifically, the same amp-hours per unit volume. More additional ferrous sampling to determine the ferrous iron oxidation rate behavior would further refine the design parameters and allow more predictable scaling of the pilot unit.

BY-PRODUCTS

Iron Oxide

In the treatment of AMD, a significant cost of the treatment can be sludge management. Thus, there is great interest in finding a use for the iron hydroxide that is generated from the treatment of high-iron flows.

There is a large market for iron oxide pigments, and the product is traded on the commodities market. In 2001 there was 69,900 metric tons of natural (mined) iron oxides produced (*Potter, 2001*). Hedin has studied the use of iron oxide from AMD in the past, and his company, Iron Oxide Recovery, Inc. has taken iron hydroxide from passive treatment systems to market as Environoxide, a series of finished pigments available through Hoover Color Group (*Hedin, 2002*). Hoover Color Group was contacted to analyze a dried and ground iron oxide from the electrolysis batch test of the Truetown site. Hoover Color Group determined that the product was usable, but had low tinting strength, a primary property needed for the use as a pigment. This loss of tinting was due to too high of drying temperature, as discovered later from the processing. This will most likely be able to be corrected, increasing the market value. Hoover's manufacturing process requires a low particle size, $<.3$ □m and moisture content less than 2%, which was achieved with drying and pulverization. Hoover's prime iron oxides that are purchased are valued at around 50 cents per pound. The electrolysis iron oxide as provided to Hoover could have a market developed for the product at around 10 to 20 cents per pound, depending on the characteristics of the delivered product and the specific market. The Truetown site produces an average of 1875 kg/day (*Riefler, 2006*), and with a value of 20 cents per pound, generates approximately $1300/day in pigment. Hoover Color Group is located in Hiwassee, VA, a 255-mile haul from the Truetown site. In addition to the logistics of hauling the material, there are also difficulties in dewatering, drying, and pulverization or grinding such quantities of sludge in a full-scale treatment scenario.

Another viable option for the use of iron hydroxide generated is in the iron salts industry. Iron salts are produced to generate iron hydroxide for the use in water treatment as a coagulant, and wastewater treatment to manage H_2S for odor control and phosphates for nutrient removal. There is a local industry growth in the production of iron salts. A facility is currently being built at PPG's Natrium, WV facility by PVS Technologies to produce 50,000 tons annually of iron salts. This facility is 110-mile haul from the Truetown site, significantly closer than Hiwassee, VA, and presents several advantages due to this industry's manufacturing process. First, the PVS Technologies process does not require a dried product, which saves some processing difficulties, although these may be offset by the additional trucking costs of hauling a wet product. Secondly, the tinting strength, which is a problem for its use as a pigment, is not of concern for its use in the production of iron salts. Testing results

from PPG revealed elevated chromium levels which deter from its use in their manufacturing. This could be addressed by a change in electrode material, as discussed in *Conclusions*.

Lastly, there is local use for a dried iron oxide for use in alloy production. Metallurg Vanadium located in Byesville, OH uses approximately 100,000 lbs per month of iron oxide for use as an oxygen supply in their manufacturing of raw supplies for alloys. Metallurg Vanadium's process requires a dried product with a maximum size of 2". The advantage of this facility's use is a shorter, 70-mile haul, and some potentially more lax requirements for their product, such as sizing and treatment residuals. The disadvantage is that a dried (<2% moisture content) is still required. Metallurg Vanadium's process requires a minimum of 50 lbs of material to run a batch test to see if the product would be a viable supplement to their current supply. Unfortunately, the pilot runs did not produce this required weight of iron for testing, and no pricing information was available at this time.

Gas Production
The electrolysis of mine drainage produces both hydrogen and oxygen gas as a by-product of the treatment, as shown in Equations #6 and #7. The volumes produced during the pilot test could not be measured because the system was not sealed, but the volumes could be significant. These two gases have the potential to be separated in a full-scale facility by placing a separate hood over each of the anodes and cathodes. The most straightforward use of these by-products would be an onsite use. First, the oxygen gas could be recirculated back through the process to increased dissolved oxygen levels (see Table 4: Pilot Project Corrosion Analysis Test) and oxidation rates. Secondly, the hydrogen gas could be used as fuel to help aid the drying process of the iron oxide. No information on the volumes produced was gathered during the pilot test due to time and logistical constraints.

20

CONCLUSIONS

Further Research Needs

Although the pilot test setup can be scaled to full treatment of AMD flows in its current configuration, the following are some items that may warrant further study:

Oxidation Rate Behavior and Components – Oxidation of the Fe^{2+} in the electrolysis unit takes place due to the anode as shown previously. This rate is also accelerated by two other factors, the O_2 gas produced on the cathode, and the catalytic oxidation due to the presence of $Fe(OH)_3$. The exact breakdown of the components of the oxidation process and their portion of the rate would be useful to understand, so that these processes could be optimized to increase the efficiency of the electrolysis treatment.

Alkaline Adjustment Materials – Sodium hydroxide was used for the entirety of the batch and pilot tests. This was used because of its controllability and consistency, but it has the disadvantage of being costly and corrosive. The use of calcium or slag products for the alkalinity adjustment may offer significant cost savings to the total treatment cost. The effluent could be recirculated back through a limestone bed or steel slag bed and fed into the electrolysis unit. With the advantage of a mostly metals free effluent that is produced by the electrolysis, there is an opportunity for the use of these materials.

Electrode Materials – Stainless steel performed well in the batch and pilot scale tests, but the anode corroded at a rate that will require plate replacement approximately every 6 months. Also, the corroded nickel and chromium were present in the iron hydroxide sludge. This may present difficulties in the marketability of the by-product. In electrochemical cells the most desired material is platinum for its stability under oxidative condition, although its use is cost prohibitive in the electrolysis of AMD. The use of carbon, graphite, carbon steel or aluminum may warrant further investigation for the use as an anode. A cost/benefit analysis would need to be performed here, as well as additional information from the iron oxide industry on whether the nickel, chromium, or aluminum concentrations affect the marketability of the iron oxide produced as a by-product of the treatment.

Conclusions

The use of electrolysis to oxidize dissolved ferrous iron is significant to the treatment of AMD because it is able to produce low effluent iron concentrations, especially in the most concentrated iron-laden flows. Conventional and even advanced oxidation processes have struggled to get iron effluent levels as low as what has been shown as a potential from the pilot tests. Hydrogen peroxide, a chemical oxidant, is very effective, but can be cost prohibitive. The electrolysis method of treatment has shown to be as effective as this combination of

treatment, and only requires electricity, minimal pumping, and an alkaline adjustment material for the operation of the electrolysis unit.

There are additional possibilities for the use of electrolysis, such as the addition of salt. The addition of salt, specifically NaCl, causes a pH rise by altering the gas production in the electrolysis cell (*Rajeshwar, 1997*). Because the oxidation of Cl⁻ has a lower standard hydrogen electrode potential than the oxidation of water, chlorine gas is produced at the anode, not oxygen, and there is a pH rise in an undivided cell due to the hydrogen gas production at the cathode. The resulting process produces chlorine gas and sodium hydroxide. This process may offer another opportunity for a material that could be used to treat AMD, and produce another marketable by product, chlorine gas. This approach would offer two significant hurdles, the accelerated corrosion of the anode in the presence of Cl⁻, and the handling of a particularly hazardous gas. Although a modification of this type to the electrolysis process would be difficult, it may warrant further study to determine feasibility.

Electrolysis is a versatile chemical treatment method that has relatively few studies with respect to its use for AMD treatment, and shows promise as other AMD treatment methods are beginning to show their true costs of long-term maintenance. Electrolysis is able to oxidize ferrous iron in a manner which is rapid, requires very little physical equipment, and produces by-products which can be either used onsite, or sold to industry. In conclusion, this study and pilot test has successfully shown that the electrolysis of mine drainage is a scalable, viable treatment method for AMD.

Post-Script
As of July 16, 2012, Ohio University and the U.S. Forest Service completed two separate test runs of AMD at the "Snake Hollow Pilot Treatment Plant". This plant is a scaled up version similar to the one constructed by ODNR, and uses electrolysis to treat 10 gpm of acid mine drainage from multiple sources. Both Snake Hollow Pilot Plant has shown successful applications of electrolysis of iron oxidation (as well as pre-treatment for aluminum removal), with the Truetown AMD producing effluent iron solids at ~97-98% purity. Dr. Guy Riefler is continuing his research into producing marketable iron pigment from this source, and early results are looking promising.

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